

FORM PTO-1390 (Modified) (REV 11-98)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER <b>1811-228 MIS:jb</b>	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR <b>09/762765</b>	
INTERNATIONAL APPLICATION NO. <b>PCT/CA99/00731</b>		INTERNATIONAL FILING DATE <b>August 11, 1999</b>		PRIORITY DATE CLAIMED <b>August 14, 1998</b>	
TITLE OF INVENTION <b>MELT PHASE HYDROSILYLATION OF POLYPROPYLENE</b>					
APPLICANT(S) FOR DO/EO/US <b>Costas Tzoganakis, et al.</b>					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
<ol style="list-style-type: none"> <li>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li>2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li>3. <input type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).</li> <li>4. <input type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.</li> <li>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371 (c) (2)) <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau).</li> <li>b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau.</li> <li>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</li> </ol> </li> <li>6. <input type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)).</li> <li>7. <input type="checkbox"/> A copy of the International Search Report (PCT/ISA/210).</li> <li>8. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3)) <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau).</li> <li>b. <input type="checkbox"/> have been transmitted by the International Bureau.</li> <li>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</li> <li>d. <input type="checkbox"/> have not been made and will not be made.</li> </ol> </li> <li>9. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</li> <li>10. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)). <i>-unsigned</i></li> <li>11. <input checked="" type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409).</li> <li>12. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).</li> </ol>					
Items 13 to 20 below concern document(s) or information included:					
<ol style="list-style-type: none"> <li>13. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</li> <li>14. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</li> <li>15. <input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment.</li> <li>16. <input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.</li> <li>17. <input type="checkbox"/> A substitute specification.</li> <li>18. <input type="checkbox"/> A change of power of attorney and/or address letter.</li> <li>19. <input type="checkbox"/> Certificate of Mailing by Express Mail</li> <li>20. <input checked="" type="checkbox"/> Other items or information:</li> </ol>					
Initial Information Data Sheet					

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.53)

097762765

INTERNATIONAL APPLICATION NO.

PCT/CA99/00731

ATTORNEY'S DOCKET NUMBER

1811-228 MIS:jb

21. The following fees are submitted:

**BASIC NATIONAL FEE ( 37 CFR 1.492 (a) (1) - (5)) :**

- ☒ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... **\$970.00**
- ☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... **\$840.00**
- ☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... **\$690.00**
- ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... **\$670.00**
- ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) ..... **\$96.00**

**ENTER APPROPRIATE BASIC FEE AMOUNT =****CALCULATIONS PTO USE ONLY****\$970.00**Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).**\$0.00**

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	22 - 20 =	2	x \$18.00	<b>\$36.00</b>
Independent claims	4 - 3 =	1	x \$78.00	<b>\$78.00</b>

Multiple Dependent Claims (check if applicable). ☐**\$0.00****TOTAL OF ABOVE CALCULATIONS =****\$1,084.00**Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable). ☐**\$0.00****SUBTOTAL =****\$1,084.00**Processing fee of **\$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).**\$0.00****TOTAL NATIONAL FEE =****\$1,084.00**Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). ☒**\$40.00****TOTAL FEES ENCLOSED =****\$1,124.00**

Amount to be:	\$
refunded	
charged	\$

☒ A check in the amount of **\$1,124.00** to cover the above fees is enclosed.

☐ Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \_\_\_\_\_ to cover the above fees.  
A duplicate copy of this sheet is enclosed.

☐ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. \_\_\_\_\_ A duplicate copy of this sheet is enclosed.

**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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24223

PATENT TRADEMARK OFFICE

SIGNATURE

Michael I. Stewart

NAME

24,973

REGISTRATION NUMBER

February 12, 2001

DATE

09/762765

JC02 Rec'd PCT/PTO 13 FEB 2001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re National Phase of International Application

No.: PCT/CA99/00731

International  
Filing Date: August 11, 1999

Applicant: Costas Tzoganakis, et al.

Title: MELT PHASE HYDROSILYLATION OF POLYPROPYLENE

Grp./A.U.:

Examiner:

Docket No.: 1811-228 MIS:jb

PRELIMINARY AMENDMENT

The Commissioner of Patents  
and Trademarks,  
Washington, D.C. 20231,  
U. S. A.

Dear Sir:

Please amend this application in the following manner:

In the Disclosure:

Immediately following the title and immediately preceding the first line of text, add to page 1:

"This application is a US National Phase filing pursuant to 35 USC 371 of International Patent Application No. PCT/CA99/00731 filed August 11, 1999."

In the Claims:

Amend claims 1 and 16 as follows:

1. (Amended) A branched copolymer of a polyolefin and a silicone polymer which is produced by melt phase reactive extrusion hydrosilylation.
16. (Amended) A blend of incompatible blend partners which are polypropylene (PP) and a methylhydrosiloxane-dimethylsiloxane random copolymer (MDMS), in which the incompatible blend partners are connected by a melt phase reactive extrusion hydrosilylation reaction in the form of a branched PP-MDMS block copolymer.

Add new claims 20, 21 and 22 as follows:

20. (New) The copolymer of claim 1 wherein said polyolefin is polypropylene.
21. (New) A process of forming a branched copolymer, which comprises:  
treating a polyolefin with peroxide to provide terminal unsaturation, and  
reacting the terminally-unsaturated polyolefin with a silicone polymer  
containing at least two Si-H groups in a melt phase reactive extrusion hydrosilylation  
reaction.
22. (New) The process of claim 21 wherein said polyolefin is polypropylene.

REMARKS/ARGUMENTS

The specification has been amended to introduce reference to the corresponding International Application of which this application is the National Phase equivalent.

Claims 1 and 16 have been amended to specify that the melt phase hydrosilylation is effected by reactive extrusion as specified, for example, in Example 4. Claim 1 has been amended to replace reference to the "polypropylene" by reference to "polyolefin", as specified on page 5, line 6. New claim 20 has been directed to the polyolefin being polypropylene. New claims 21 and 22 have been added, directed to the two-step manufacturing process, described on page 8.

Attached hereto is a mark-up version of the changes made to the specification and claims by the current amendment. The attached page is captioned "Version with markings to show changes made".

Respectfully submitted



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Date: February 12, 2001

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**VERSION WITH MARKINGS TO SHOW CHANGES MADE**

**In the Specification:**

Immediately following the title and immediately preceding the first line of text, add to page 1:

“This application is a US National Phase filing pursuant to 35 USC 371 of International Patent Application No. PCT/CA99/00731 filed August 11, 1999.”

**In the Claims:**

Amend claims 1 and 16 as follows:

1. (Amended) A branched copolymer of a polyolefin [~~polypropylene (PP)~~] and a silicone polymer which is produced by melt phase reactive extrusion hydrosilylation.
16. (Amended) A blend of incompatible blend partners which are polypropylene (PP) and a methylhydrosiloxane-dimethylsiloxane random copolymer (MDMS), in which the incompatible blend partners are connected by a melt phase reactive extrusion hydrosilylation reaction in the form of a branched PP-MDMS block copolymer.

Add new claims 20, 21 and 22 as follows:

20. (New) The copolymer of claim 1 wherein said polyolefin is polypropylene.
21. (New) A process of forming a branched copolymer, which comprises:  
treating a polyolefin with peroxide to provide terminal unsaturated, and  
reacting the terminally-unsaturated polyolefin with a silicone polymer containing at least two Si-H groups in a melt phase reactive extrusion hydrosilylation reaction.
22. (New) The process of claim 21 wherein said polyolefin is polypropylene.

THE UNIVERSITY OF CHICAGO

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### Correspondence Information

## Application Information

## Representative Information

## Continuity Information

This application is a: National Phase of  
Application One: PCT/CA99/00731  
Filing Date: August 11, 1999

TITLE OF INVENTIONMELT PHASE HYDROSILYLATION OF POLYPROPYLENE

5

FIELD OF INVENTION

The present invention relates to the hydrosilylation of polypropylene and other polymers, particularly at terminal double bonds provided therein, to provide branched chain structures.

10

BACKGROUND TO THE INVENTION

Hydrosilylation of vinyl-terminated polypropylene (PP) has proven to be a suitable method to prepare end-functional polymers. These techniques can be used for the compatibilization of inorganic fillers or polymer blends. In WO 97/47665, assigned to University of Waterloo and the disclosure of which is incorporated herein by reference, it has been shown that the hydrosilylation of the polymer can be performed in the melt phase, that is during processing, when a platinum catalyst is activated by a peroxide. WO 97/47665 specifically describes the preparation of linear structures, i.e. the preparation of polypropylene-polydimethylsiloxane (PDMS) block copolymers. This result was achieved (WO 97/47665) by reaction of a vinyl-terminated PP with a mixture of a hydride-terminated polydimethyl-siloxane/Pt/t-butylhydroperoxide solution in a batch mixer or single-screw extruder at processing temperatures of about 170° to about 220°C. Thus, melt phase hydrosilylation makes it possible to produce PP-PDMS block copolymers. This product is of considerable interest since it is known that polydimethylsiloxanes have a low glass transition temperature and a high gas permeability. By in-situ synthesis of block copolymers, reactive blending of

both polymers becomes possible and thus interesting blend properties can be achieved.

However, to prepare the vinyl-termination on the chain-end necessary for the preparation of the block  
5 copolymers, the polypropylene was degraded by peroxides prior to the hydrosilylation reaction. The degradation has led to a decrease in the molar mass as well as in the polydispersity. These effects reduced the mechanical properties of the material, such as the  
10 elongation at break and the tensile impact strength. Hence, the application of the products produced according to the procedures of WO 97/47665, was restricted.

#### SUMMARY OF INVENTION

15 It has now been found that the detrimental effects of the terminal degradation, namely decrease of molar mass and polydispersity, can be reversed by reacting, in the melt phase, vinyl-terminated polypropylene with, for example, a methyl hydrosiloxane-dimethylsiloxane  
20 random copolymer (MDMS). In general, a polysilane having at least two Si-H groups and sufficient to permit the generation of a three-dimensional or branched structure is employed.

In accordance with one aspect of the present  
25 invention, there is provided a branched copolymer of polypropylene (PP) or other polymer and a silicone polymer. Such copolymers may be formed by melt phase hydrosilylation of terminally-unsaturated polypropylene or other polymer containing unsaturation.

30 The silicone polymer may be various linear, branched and cyclic polysilanes as discussed in detail below. The copolymers provided herein may be useful for fibre spinning, thermoforming, blow molding and/or thermoforming applications.



In one specific embodiment of the invention, the silicone polymer is a methylhydrosiloxane-dimethylsiloxane (MDMS) random block copolymer. The PP and MDMS may be reacted in such a ratio as to leave  
5 free Si-H groups in the polymer. Such free Si-H groups may be used to couple the copolymer to a variety of other materials, including inorganic fillers, inorganic surfaces, hydroxy-containing polymers, vinyl-containing polymers or other polymers containing functional groups  
10 reactive with free Si-H groups.

The coupling between the copolymer having free Si-H groups and the other materials may be effected in any convenient manner, generally by a hydrosilylation reaction or a dehydrogenerative coupling reaction,  
15 depending on the nature of the coupling.

Alternatively, in a copolymer with free Si-H groups, such Si-H groups may be cross-linked. Such cross-linking may be effected by converting Si-H groups to Si-OH groups by a metal catalyzed reaction with  
20 water and subsequently dehydrogeneratively coupling to other free Si-H groups. Alternatively, the free Si-H groups may be reacted with dehydrogenerative coupling.

The PP-MDMS copolymer also may be coupled to metallic, glass, ceramic or other vitreous surfaces.

25 Polypropylene and silicone polymers are normally incompatible to blend together. The present invention enables stable blends to be provided. Accordingly, in a further aspect of the invention, there is provided a blend of incompatible blend partners which are  
30 polypropylene (PP) and a silicone polymer, which may be rendered compatible by forming a branched copolymer, preferably by a hydrosilylation reaction. Alternatively, the incompatible blend partners are connected by Si-O-Si bridges.

The silicone polymer preferably is a methylhydrosiloxane-dimethylsiloxane random copolymer (MDMS), which is incorporated into a branched PP-MDMS block copolymer by melt phase hydrosilylation. The PP-MDMS  
5 block copolymer may contain free Si-H groups.

The present invention further extends to a method of forming a branched polypropylene or other polymer, which comprises effecting melt phase hydrosilylation of terminally-unsaturated polypropylene or other polymer  
10 containing unsaturation in the presence of methylhydrosiloxane-dimethylsiloxane random copolymer (MDMS).

In addition, the present invention provides, in a further aspect, a process of forming a branched  
15 polypropylene or other polymer, which comprises:

effecting dehydrosilylation of a vinyl end group of polypropylene or other unsaturated polymer and a trialkoxysilane to form a functionalized polymer, and  
thereafter effecting post-reaction branching of  
20 the functionalized polymer by reacting Si-OR groups to form a Si-O-Si bridge.

#### BRIEF DESCRIPTION OF DRAWINGS

Figure 1 contains a graphical representation of the relationship of torque to kneading time in an  
25 experiment described herein;

Figures 2 and 3 contain the graphical representations of the results of oscillatory shear experiments carried out on polymers produced herein.

Figures 4 to 6 contain graphical representations  
30 of the results of mechanical testing of the polymers produced herein.

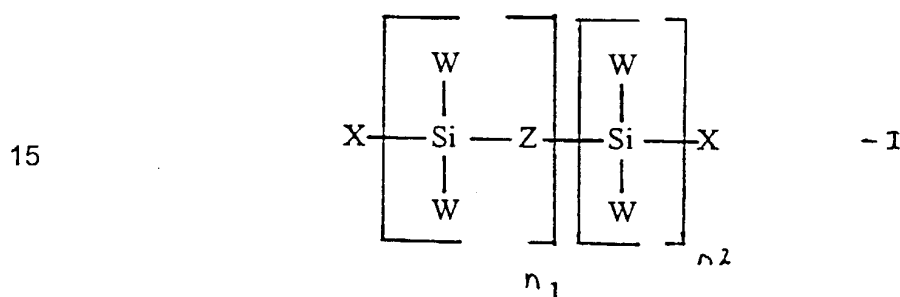
#### GENERAL DESCRIPTION OF INVENTION

As set forth above, the present invention is concerned with a melt phase hydrosilylation of

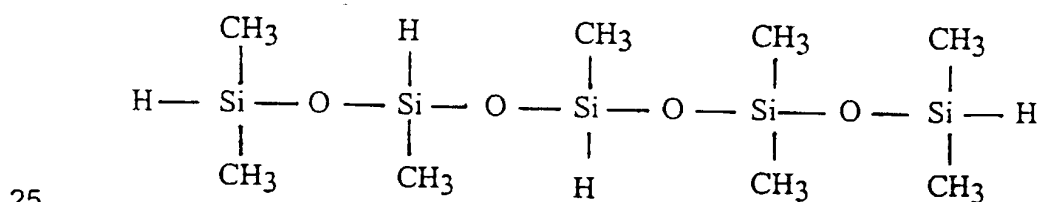
polypropylene with polysilane having at least two Si-H groups and sufficient to permit the generation of a three-dimensional or branched structure.

Although the invention is described herein with reference to polypropylene, the hydrosilylation process is applicable to all types of polyolefins or indeed any other polymer which is inert to the conditions of the hydrosilylation reaction and in which double bonds are present.

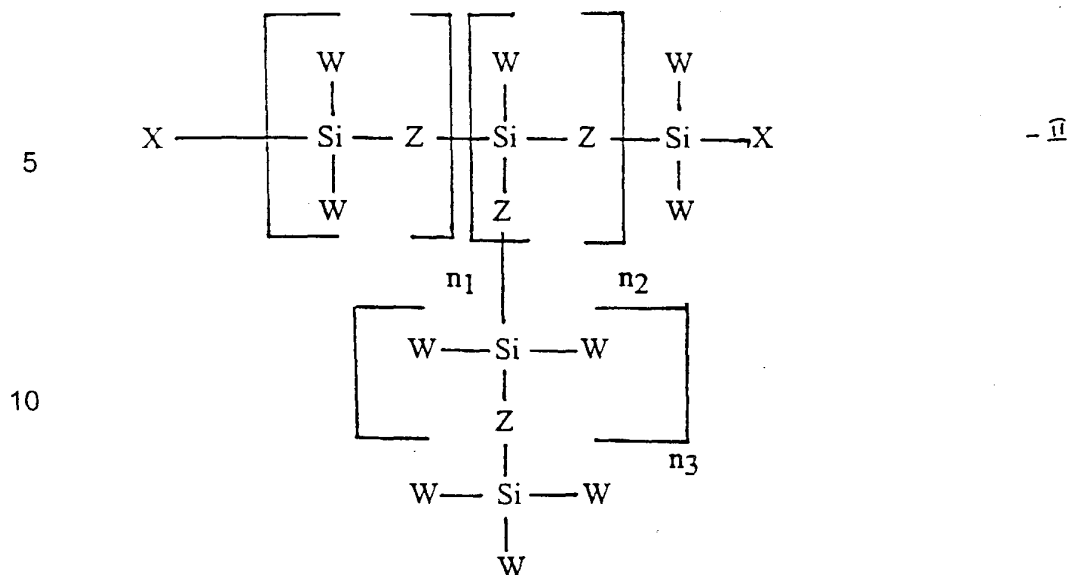
One class of polysilane which may be employed herein has the Formula I:



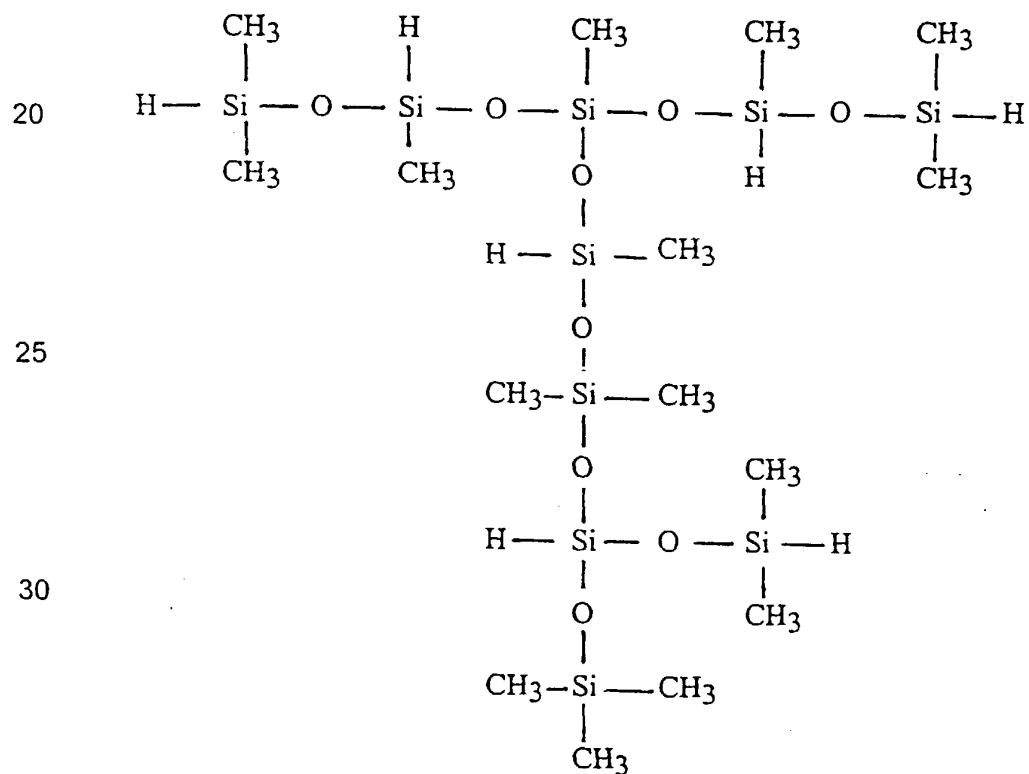
An example of a polysilane according to Formula I is the polyhydrosiloxane having the formula:



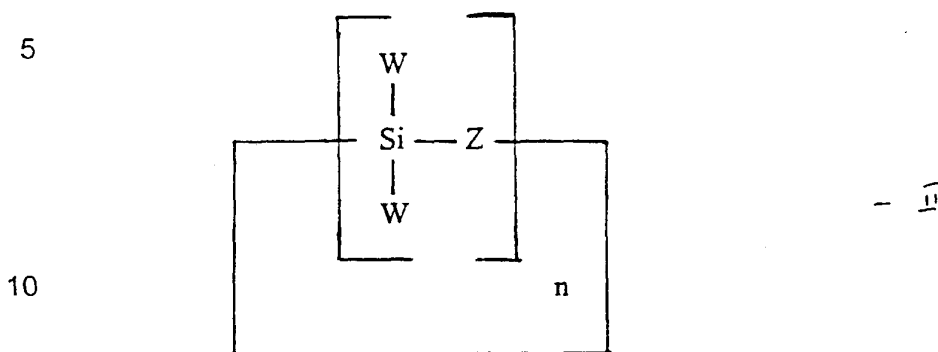
Another class of polysilane which may be employed herein has the Formula II:



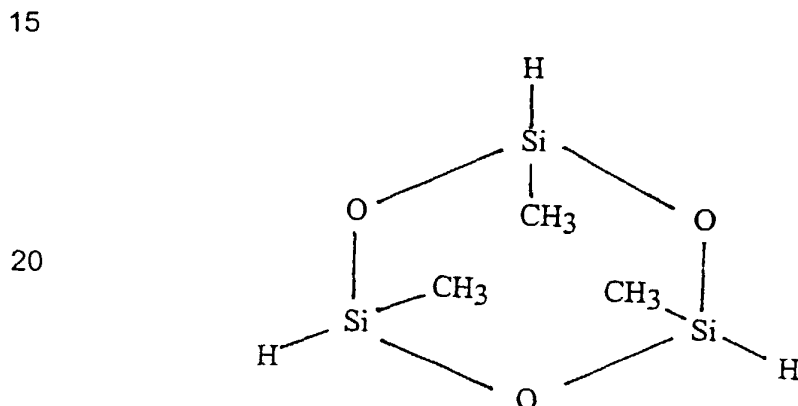
15 An example of a polysilane according to Formula II is the branched polyhydrosiloxane having the formula:



A further class of polysilane which may be employed herein has the Formula III:



An example of a polysilane according to Formula III is the cyclic polyhydrosiloxane having the formula:



25 In the above Formulae I, II and III, the symbols mean as follows:

X is any organic end group and preferably is  $-\text{CH}_3$  or  $-\text{H}$ ;

30 W is any organic or inorganic group. Typical examples for W are H,  $\text{CH}_3$ , alkyl, phenyl, amines, nitriles, halides, silicones, siloxanes.

X and W are selected to ensure that the molecule contains at least two Si-H groups and sufficient to provide a branched structure.

n,  $n_1$  or  $n_2$  is the number of repeating groups in the chain. In addition, branched polypropylene can also be produced by the use of any branched silane or siloxane or any other two or three dimensional silane or siloxane structure, such as rings or cubes, for example, a three-dimensional silsesquioxane.

The present invention is concerned with the functionalization of terminal double bonds in polypropylene and other polymers to yield a branched block copolymer structure. The terminal double bonds in polypropylene are created by peroxide degradation. The use of any other polypropylene with terminal vinylidene radicals (i.e., Metallocene PP, amorphous PP) is possible. The functionalization is performed by peroxide-initiated or platinum-catalyzed hydrosilylation. In the case of the platinum-catalyzed hydrosilylation reaction, t-butylhydroperoxide may be added as a cocatalyst. The reactions are performed in the melt phase of the polypropylene in typical processing equipment, i.e., an extruder, a batch mixer or other convenient equipment, such as a hot press. The reaction conditions are such that conversion of the reactants is high during the processing. Once the product leaves the equipment, no further treatment, such as curing or purifying is necessary. Degradation of the polypropylene to provide terminal unsaturation and hydrosilylation with the appropriately hydrided polysilane can be performed simultaneously or sequentially without intermittent solidification, as well as sequentially with intermittent solidification, as desired.

We have shown by experimentation that the formation of MDMS-PP branch copolymers leads to an increase in molar mass as well as polydispersity. In

one typical experiment, 3g of toluene were added to 1.5g MDMS with a molar mass of 2000 and an Si-H content of about 25 to 30 mol% SiH. After addition of 45 $\mu$ L of platinum catalyst (Karstedt's catalyst - platinum (O)-divinyl-tetramethyldisiloxane) and 90 $\mu$ L of cumene hydroperoxide, the solution was masterbatched with 35g of degraded Polypropylene (PP-deg). Subsequently the mixture was kneaded in a Brabender mixer for 60 min. at 180°C. In that time the torque of the kneader increased significantly (Fig.1). The product of the reaction was investigated by high temperature (HT) gas phase chromatography (GPC). The result obtained is shown in Table 1 below. Clearly, an increase in molar mass and polydispersity compared to the degraded PP can be seen. The sample was soluble in toluene which indicates that a branched structure was produced rather than a cross linked structure. When interpreting the GPC data, it has to be considered that this technique underestimates the molar mass of branched structures. This is caused by the smaller hydrodynamic volume of these branched molecules.

A sample of the product was investigated in oscillatory shear experiments. The results are summarized in Fig. 2 and Fig. 3. The complex viscosity of the PP-MDMS material is dramatically increased compared to the degraded PP (Fig. 2). In addition, the PP-MDMS material appears to be more elastic than both the virgin PP (Novolen) and the degraded PP (its storage modulus is higher than that of the other two materials, as seen in Fig. 3). The improved elasticity of the material makes it a very good candidate for fibre spinning, thermoforming, blow molding, and foaming applications.

The PP-MDMS polymer produced in this experiment

could not be dissolved by THF from the sample blends, suggesting that the PP-MDMS was acting as a compatibilizer. The PP-MDMS could only be removed by depolymerization. To investigate this issue, a  
5 microtomed surface was treated with 20% KOH for 5 h at 60°C to depolymerize the siloxane. Afterwards, the samples were investigated by scanning electron microscopy and small holes (1µm or less in diameter) were observed, proving the removal of the MDMS phase.

10 In another experiment, 9 wt% of MDMS were reacted with the degraded PP. Samples of the blends were injection moulded into a dog-bone shaped specimen (S2 Din 53 504) and submitted to mechanical testing. As it can be seen in Fig. 4 to Fig. 6, all mechanical  
15 characteristics of the hydrosilylated product increased significantly. Although the MDMS is a liquid with a low viscosity it did not show the effect of a plasticizer. This can be seen in Fig. 5.

These experiments show that the formation of  
20 branched PP-MDMS block copolymers with good mechanical properties is possible following the procedure of the invention. If Si-H groups are used in excess of those required to provide the branched structure, then this gives the opportunity for further reactions. For  
25 example, the Si-H group may be readily transformed into another functional group, such as an Si-OH by reaction with water. Reaction of such Si-OH groups with alcohols by dehydrogenative coupling leads to the formation of silylethers. If the hydroxy groups on the  
30 silylethers were coupled to another polymer, this would mean another compatibilization reaction. If the hydroxy-groups on the silylether are part of the surface of an inorganic filler, the coupling of the PP to the filler may be enhanced.



Functionalization of vinyl-terminated PP with a silane bearing hydrolysable groups leads to a second but indirect pathway to producing a branched polypropylene. Examples of silane for use in producing such a PP are trimethoxysilane, triethoxysilane and trichlorosilane. In this procedure, a PP is hydrosilylated in the melt phase with the triethoxysilane, for example. The resulting alkoxyether may be hydrolysed by boiling the sample in a waterbath. Addition of a metal catalyst, such as dibutyl tin laurate, activates the hydrolysis. At the same time, the catalyst catalyses the condensation of two Si-OH groups produced by the hydrolysis reaction to form an Si-O-Si bridge, leading to a branching of PP chains. A sample of such a reaction pathway was investigated by HT-GPC. The results are summarized in Table 1. Again an increase in  $M_w$  and  $M_z$  can be seen.

Table 1

Materials	Mn (g/mol)	Mw (gfmol)	Mz (gfmol)
Degraded PP	31000	72000	135000
PP-MDMS	47000	210000	720000
PP-Triethoxysilane	30000	88000	450000

EXAMPLES

Example 1:

This Example describes the formation of the reactive MDMS/Pt solution used to hydrosilylate polypropylene.

9 g of toluene were added to 6g of a MDMS (HMS 301- Gelest. Corp. molecular mass 2000. 40 $\mu$ L platinum catalyst and 200  $\mu$ L cumene hydroperoxide next were

added under vigorous stirring of the solution. After the gas formation stopped, the solution was blanketed with argon and stored in the refrigerator.

Example 2

5        This Example describes the degradation of the polypropylene which is used for the melt phase hydrosilylation.

3kg PP (Novolen 1127 N-BASF, Mwt. were masterbatched with 0.5 wt% of DHBP (dihydro-  
10 butylperoxide -Peroxide Chemie) in a 5 L powder bottle. The masterbatch was loaded into a hopper and fed to a twin screw extruder (ZSK 30. Werner and Pfleiderer). The reaction temperature was 220°C. The extruder screw speed was 200 RPM and the product was extruded through  
15 a 4 mm die and was pelletized after cooling in a water bath.

Example 3:

This Example describes the formation of branched PP-MDMS copolymers in a Brabender-Mixer.

20        35g granules of PP (deg) were mixed with 5g of powdered PP (deg). 4g of the solution described in sample 1 were added to the PP (deg). The masterbatch was fed to a brabender mixer at 180°C and kneaded with 80 RPM. The torque of the brabender was followed on-  
25 line.

After 60 min. the reaction was stopped and the product was recovered.

Example 4

30        This example describes the formation of a branched PP-MDMS copolymer in a reactive extrusion step.

PP (deg) from Example 2 was added to a Haake Rheomex 252 single screw extruder until steady state was reached. Then 100g of a masterbatch of PP (deg) and 3 wt% of MDMS/toluene/Pt/cumene hydroperoxide solution

from Example 1 were added to the feeder.

The reaction was observed until steady state was reached. Then, it was allowed to proceed for another 10 min.

5 Example 5

This Example describes the formation of a glass fibre reinforced PP-MDMS-blend in a Brabender mixer.

35g granules of PP (deg) were mixed with 5g of powdered PP (deg). 8g of the solution described in  
10 sample 1 were added to the PP (deg). The masterbatch was loaded to a Brabender mixer at 180°C and kneaded at 80 RPM. The torque of the brabender was followed on-line.

After 60 min, 10g of glass fibres were added to  
15 the system. The mixture was kneaded until the product was homogeneous and then stopped. The product was recovered.

Example 6

This Example describes the synthesis of a  
20 triethoxysilane-Pt solution used to hydrosilylate PP.

100 µL Pt-catalyst and 200 µL cumene hydroperoxide were added to 10g triethoxysilane. The mixture was stirred until the gas development stopped. The solution was blanketed with argon and stored at 5°C.

25 Example 7

This Example describes the formation of a branched PP polymer.

3g of powdered PP (deg) of Example 2 were masterbatched with 0.3 ml of a solution prepared as  
30 described in Example 6. The masterbatch was added to a minimixer. The reaction was allowed to proceed at 170°C for 30 min.

The recovered product was boiled in a solution consisting of 5g isopropanol, 89g water and 1g dibutyl tin laurate to lead to a branching of the PP.

SUMMARY OF THE DISCLOSURE

5        In summary of this disclosure, the present invention provides procedures for obtaining branched polypropylene-polysilane copolymers by the use of specific polysilanes in melt phase hydrosilylation reactions. Modifications are possible within the scope  
10 of the invention.

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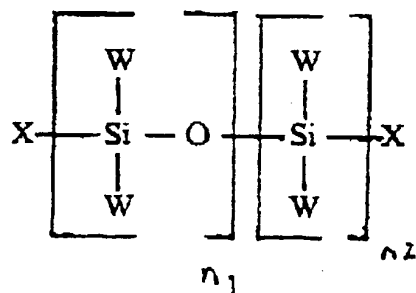
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CLMS

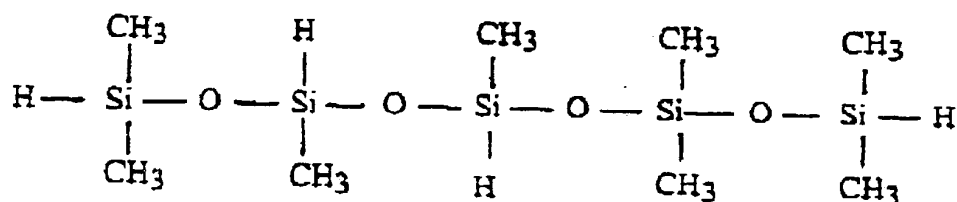
# CLAIMS

1. A branched copolymer of polypropylene (PP) and a silicone polymer which is produced by melt phase hydrosilylation.
2. The copolymer of claim 1 wherein said silicone polymer is a polysilane of the Formula I:



wherein X is an organic end group, W is an organic or inorganic group, with X and W being selected such that the polysilane contains at least two Si-H groups and sufficient to provide a branched structure, and  $n_1$  and  $n_2$  are the number of repeating groups in the chain.

3. The copolymer of claim 2 wherein said polysilane of formula I is a polyhydrosiloxane of the formula:



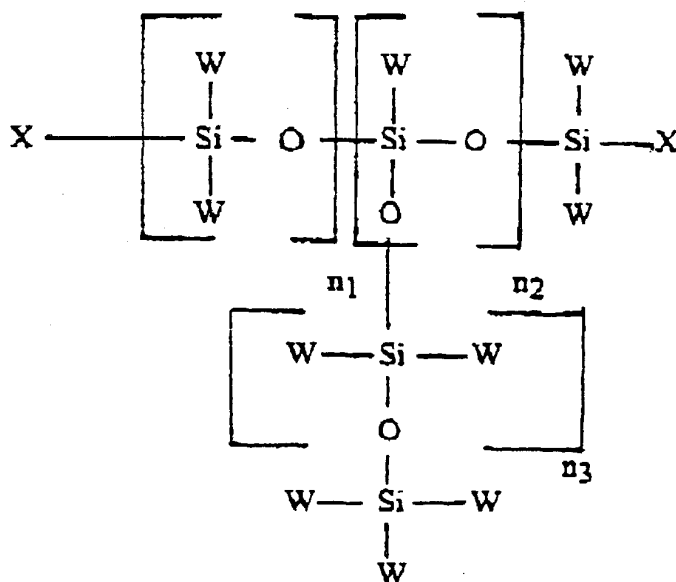
4. The copolymer of claim 1 wherein said silicone polymer is a polysilane of the Formula II:

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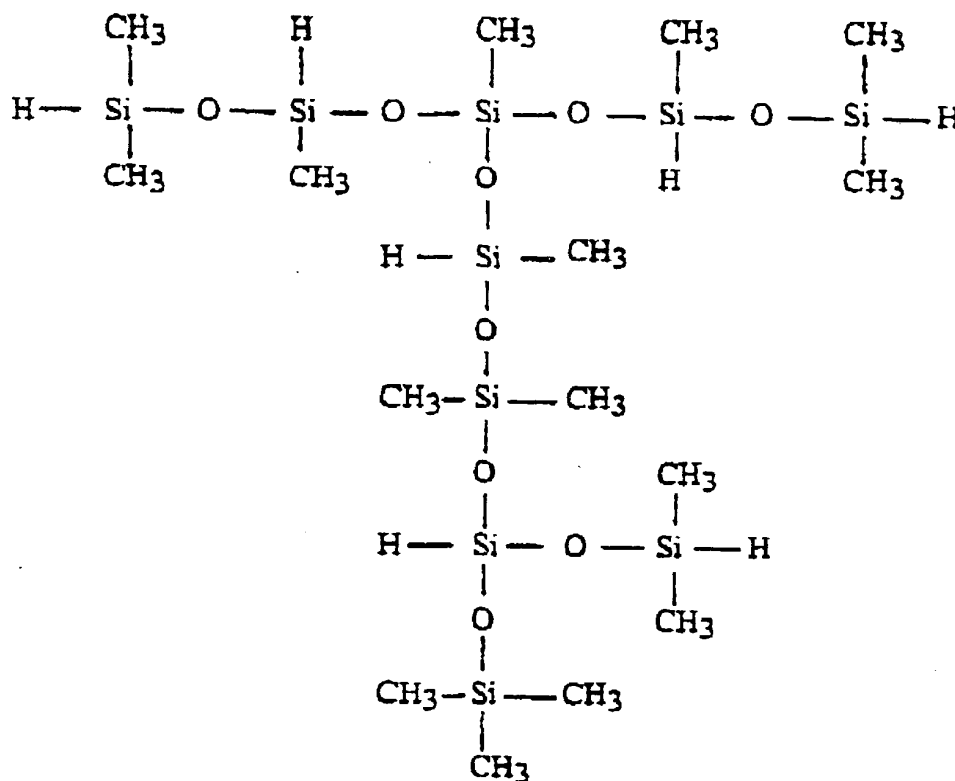
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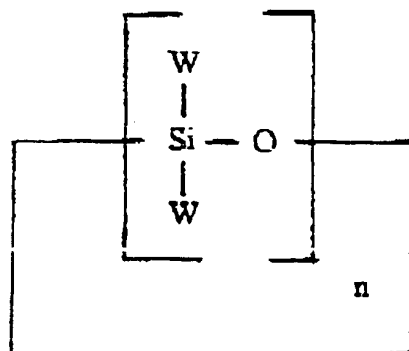
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wherein X is an organic end group, W is an organic or inorganic group, with X and W being selected such that the polysilane contains at least two Si-H groups and sufficient to provide a branched structure, and  $n_1$ ,  $n_2$  and  $n_3$  are the number of repeating groups in the chain.

5. The copolymer of claim 4 wherein said polysilane of Formula II is a branched polyhydrosiloxane of the formula:



6. The copolymer of claim 1 wherein said silane polymer is a polysilane of the formula III:



III

wherein W is an organic or inorganic group selected such that the polysilane contains at least two Si-H groups and sufficient to provide a branched structure, and n is the number of repeating groups in the chain.

7. The copolymer of claim 6 wherein said polysilane

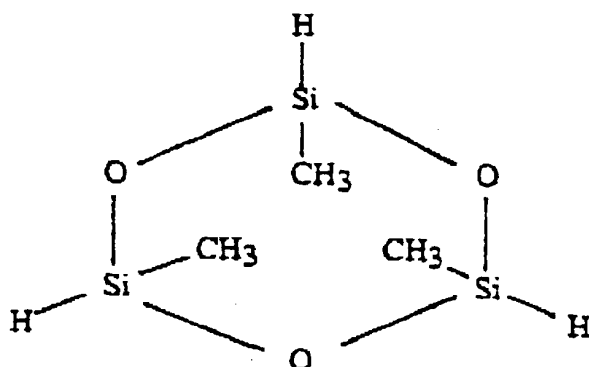
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is a cyclic polyhydrosiloxane of the formula:



8. The copolymer of claim 1 wherein said silicone polymer is a methylhydrosiloxane-dimethylsiloxane random copolymer (MDMS).

9. The copolymer of claim 8 wherein the ratio of PP to MDMS is such that the copolymer contains free Si-H groups.

10. The copolymer of claim 9 which is coupled, through free Si-H groups, to an inorganic filler, inorganic surface, a hydroxy-containing polymer, vinyl-containing polymer or other polymer containing functional groups reactive with free Si-H.

11. The copolymer of claim 10 wherein said coupling is effected by a hydrosilylation reaction or a dehydrogenerative coupling reaction.

12. The copolymer of claim 9 wherein the free Si-H groups are cross-linked.

13. The copolymer of claim 12 wherein free Si-H groups are connected into a Si-OH group by a metal-catalyzed reaction with water and subsequently dehydrogenatively coupling to a second Si-H group.

14. The copolymer of claim 12 wherein Si-H groups are reacted by dehydrogenative coupling.

15. The copolymer of claim 8 which is coupled to metallic, glass, ceramic or other vitreous surface.



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16. A blend of incompatible blend partners which are polypropylene (PP) and a methylhydrosiloxane-dimethylsiloxane random copolymer (MDMS), in which the incompatible blend partners are connected by a hydrosilylation reaction in the form of a branched PP-MDMS block copolymer.

17. The blend of claim 16 containing free Si-H groups.

18. A process of forming a branched polypropylene, which comprises effecting melt phase hydrosilylation of a terminally-unsaturated polypropylene in the presence of a methylhydrosiloxane-dimethylsiloxane random copolymer (MDMS).

19. A process of forming a branched polypropylene, which comprises:

effecting hydrosilylation at a vinyl end of polypropylene with a trialkoxysilane to form a functionalized polymer, and

thereafter effecting post-reaction branching of the functionalized polymer by reacting Si-OR groups to form a Si-O-Si bridge.

**PCT**

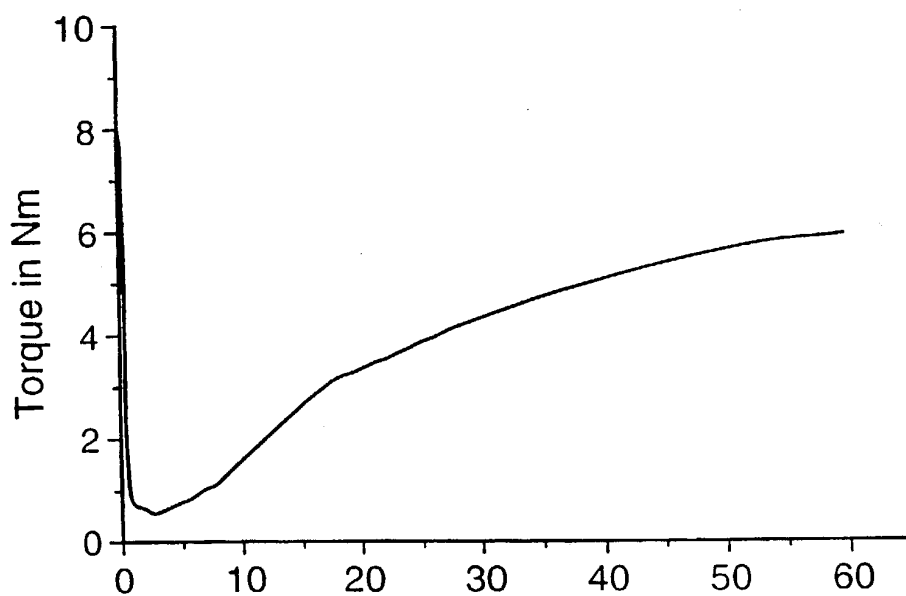
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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/CA99/00731 <b>(22) International Filing Date:</b> 11 August 1999 (11.08.99) <b>(30) Priority Data:</b> 60/096,650 14 August 1998 (14.08.98) US <b>(71) Applicant (for all designated States except US):</b> UNIVERSITY OF WATERLOO [CA/CA]; Waterloo, Ontario N2L 3G1 (CA). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> TZOGANAKIS, Costas [CA/CA]; 49 Rauch Court, Kitchener, Ontario N2N 3C8 (CA). MALZ, Hauke [DE/DE]; Schleslerstrasse 68, D-49356 Diepholz (DE). <b>(74) Agent:</b> STEWART, Michael, I.; Sim & McBurney, 6th floor, 330 University Avenue, Toronto, Ontario M5G 1R7 (CA).		<b>(81) Designated States:</b> CA, JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> MELT PHASE HYDROSILYLATION OF POLYPROPYLENE  <b>(57) Abstract</b> <p>Branched copolymers of polypropylene (PP) and polysilanes are prepared by procedures involving melt phase hydrosilylation. Such branched copolymers may be formed <i>in situ</i> during the melt phase hydrosilylation or may be prepared by subsequent processing. The branched copolymers exhibit superior properties.</p>		

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t in min  
FIG.1

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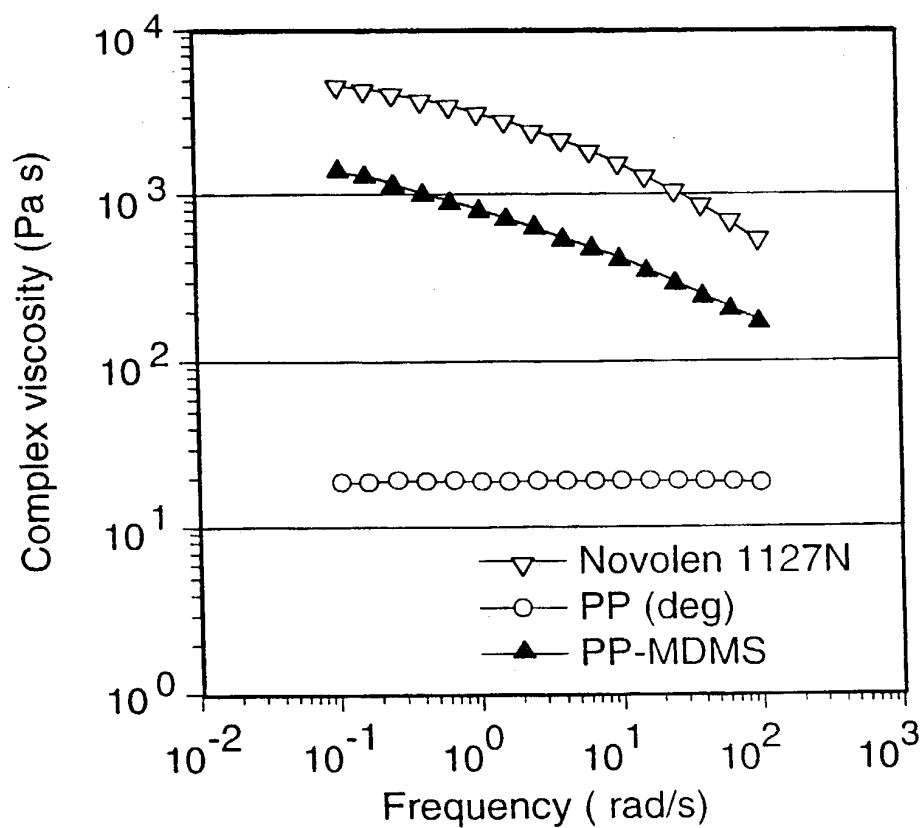


FIG.2

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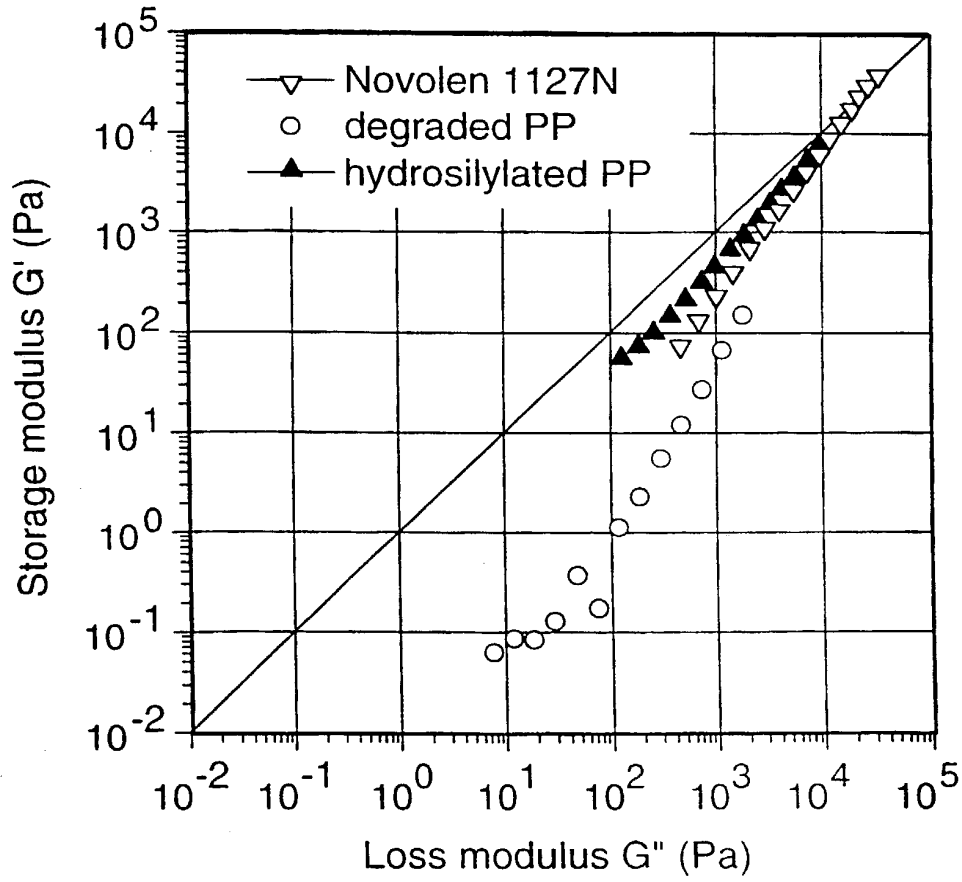


FIG.3

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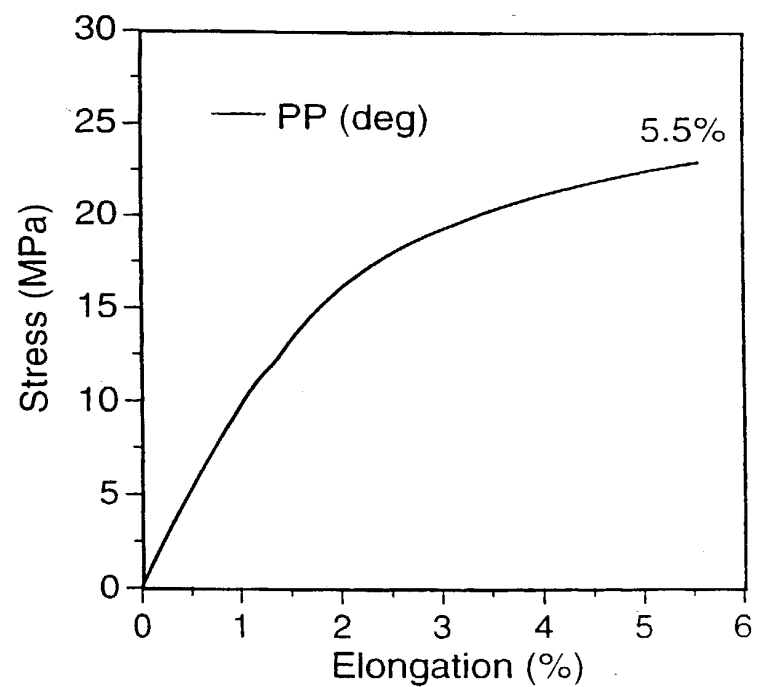


FIG.4A

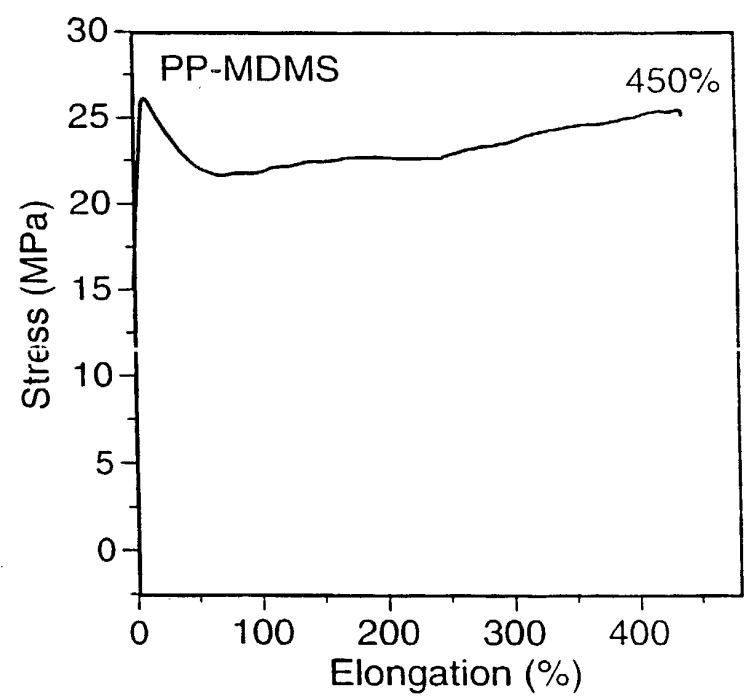


FIG.4B

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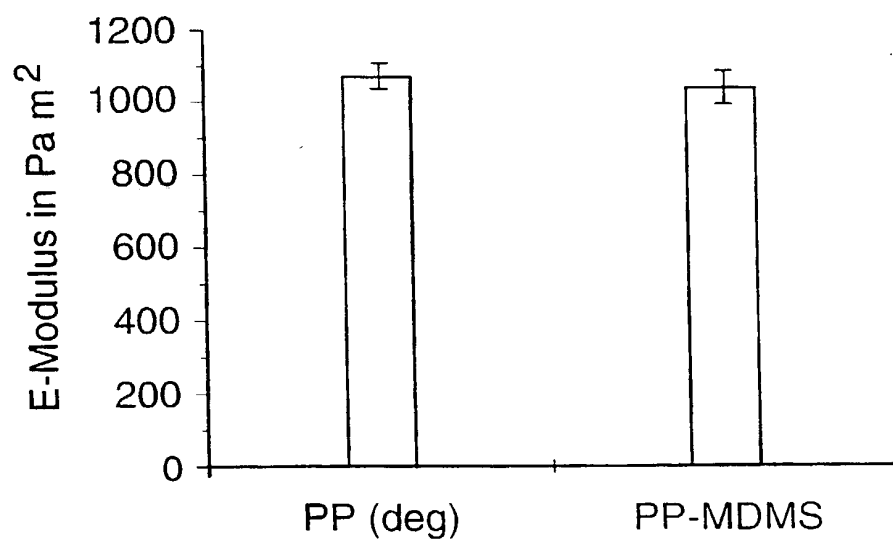


FIG.5

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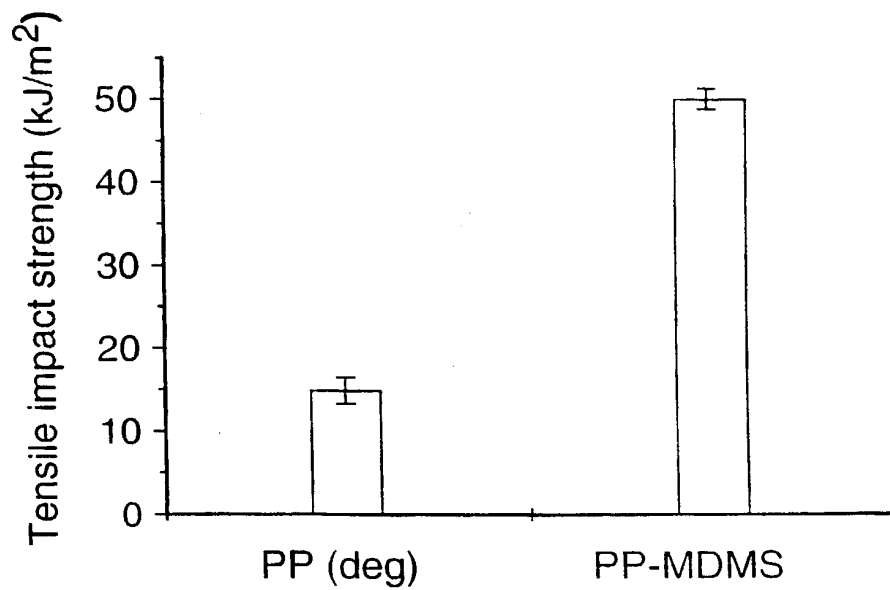
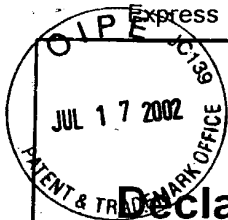


FIG.6



Docket No.  
1811-228 MIS



## Declaration and Power of Attorney For Patent Application

### English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

**MELT PHASE HYDROSILYLATION OF POLYPROPYLENE**

the specification of which  
(check one)

☐ is attached hereto.

☒ was filed on August 11, 1999 as United States Application No. or PCT International Application Number PCT/CA99/00731

and was amended on \_\_\_\_\_

(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

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Prior Foreign Application(s)

Priority Not Claimed

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(Number) (Country) (Day/Month/Year Filed)

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(Number) (Country) (Day/Month/Year Filed)

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60/096,650	August 14, 1998
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POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (list name and registration number)

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